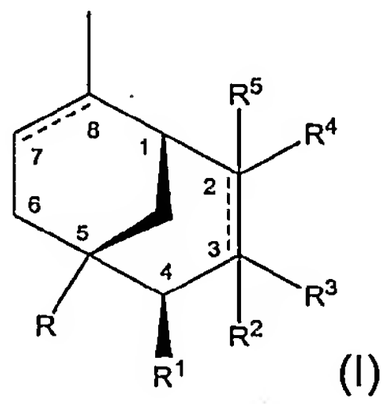
ORGANIC COMPOUNDS

The present invention relates to substituted bicyclo[3.3.1]nonanes and bicyclo[3.3.1]nonenes, having ambery, woody odour notes. This invention relates furthermore to a method of their production and to flavour and fragrance compositions comprising them.

In the fragrance industry there is always an ongoing demand for new compounds that enhance or improve on odour notes, or impart new odour notes.

Surprisingly, we have found a novel class of compounds having much sought-after ambery woody odour notes and which may be produced from readily-available cheap and naturally available starting materials.

In a first aspect the invention refers to a compound of formula (I)



(I)

wherein

R is isopropyl or iso-propenyl;

R^1 is hydrogen, methyl or ethyl;

R^2 and R^3 are independently hydrogen, methyl, or ethyl: or

R^2 and R^3 taken together is ethylidene; or

R^2 and R^3 taken together is a divalent radical $(CH_2)_2$ which forms cyclopropane together with the carbon atom to which they are attached;

R^4 and R^5 are independently hydrogen, hydroxy, C_1 to C_3 alkoxy, e.g. methoxy, ethoxy, or C_2 to C_3 acyloxy, e.g. acetoxy; or

R^4 and R^5 together with the carbon atom to which they are attached form a 1,3-dioxolane ring or a 1,3-dioxane ring; or

R^4 and R^5 together with the carbon atom to which they are attached form a carbonyl group;
the bond between C2 and C3 is a single bond, or the dotted line together with the bond between C2 and C3 represents a double bond; and
the bond between C7 and C8 is a single bond, or the dotted line together with the bond between C7 and C8 represents a double bond.

The compounds according to the present invention contain several chiral centres and as such may exist as a mixture of stereoisomers, or they may be resolved as isomerically pure forms. Resolving stereoisomers adds to the complexity of manufacture and purification of these compounds and so it is preferred to use the compounds as mixtures of their stereoisomers simply for economic reasons. However, if it is desired to prepare individual stereoisomers, this may be achieved according to methodology known in the art, e.g. preparative HPLC and GC or by stereoselective syntheses.

Particular preferred compounds of formula (I) are 5-isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-one; 4-ethyl-5-isopropenyl-8-methylbicyclo[3.3.1]non-7-en-2-one; 5-isopropenyl-3,4,8-trimethylbicyclo[3.3.1]non-7-en-2-one; 5-isopropenyl-3,3,4,8-tetramethylbicyclo[3.3.1]non-7-en-2-one; 5-isopropenyl-8,8-dimethoxy-2,6-dimethylbicyclo[3.3.1]non-2-ene; 4,8-dimethyl-5-isopropenylspiro[bicyclo[3.3.1]nonane-2,2'-[1,3]dioxolane]; 5-isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-ol; 5-isopropenyl-2,4,8-trimethylbicyclo[3.3.1]non-7-en-2-ol; 5-isopropyl-4,8-dimethylbicyclo[3.3.1]nonan-2-one, 5-isopropenyl-8-methylbicyclo[3.3.1]non-7-en-2-one, 5-isopropenyl-3,4,8-trimethylbicyclo[3.3.1]non-7-en-2-one, and 4,8-dimethyl-5-isopropenyl-8-methoxy-bicyclo[3.3.1]non-7-ene.

The compounds according to the present invention may be used alone or in combination with a base material. As used herein, the "base material" includes all known odourant molecules selected from the extensive range of natural and synthetic molecules currently available, such as essential oils, alcohols, aldehydes and ketones, ethers and acetals, esters and lactones, macrocycles and heterocycles, and/or in admixture with one or more ingredients or excipients conventionally used in conjunction with odourants in fragrance compositions, for example, carrier materials, and other auxiliary agents commonly used in the art.

The following list comprises examples of known odourant molecules, which may be combined with the compounds of the present invention:

– ethereal oils and extracts, e.g. tree moss absolute, basil oil, castoreum, costus root oil, myrtle oil, oak moss absolute, geranium oil, jasmin absolute, patchouli oil, rose oil, sandalwood oil , wormwood oil, lavender oil or ylang-ylang oil;

– alkohols, e.g. citronellol, Ebanol™, eugenol, farnesol, geraniol, Super Muguet™, linalool, phenylethyl alcohol, Sandalore™, terpineol or Timberol™.

– aldehydes and ketones, e.g. α-amylcinnamaldehyd, Georgywood™, hydroxycitronellal, Iso E Super®, Isoraldeine®, Hedione®, maltol, methyl cedryl ketone, methylionone or vanillin;

– ether and acetals, e.g. Ambrox™, geranyl methyl ether, rose oxide or Spirambrene™.

– esters and lactones, e.g. benzyl acetate, cedryl actetate, γ-decalactone, Helvetolide®, γ-undecalactone or vetivenyl acetate.

– macrocycles, e.g. ambrettolide, ethylene brassylate or Exaltolide®.

– heterocycles, e.g. isobutylchinoline.

The compounds of the present invention may be used in a broad range of fragrance applications, e.g. in any field of fine and functional perfumery, such as perfumes, household products, laundry products, body care products and cosmetics. The compounds can be employed in widely varying amounts, depending upon the specific application and on the nature and quantity of other odourant ingredients. The proportion is typically from 0.001 to 20 weight percent of the application. In one embodiment, compounds of the present invention may be employed in a fabric softener in an amount of from 0.001 to 0.05 weight percent. In another embodiment, compounds of the present invention may be used in fine perfumery in amounts of from 0.1 to 20 weight percent, more preferably between 0.1 and 5 weight percent. However, these values are

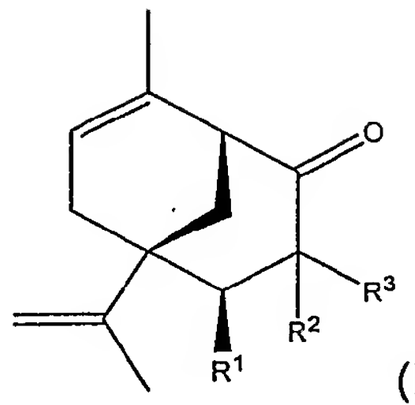
given only by way of example, since the experienced perfumer may also achieve effects or may create novel accords with lower or higher concentrations.

The compounds of the present invention may be employed into the fragrance application simply by directly mixing the fragrance composition with the fragrance application, or they may, in an earlier step be entrapped with an entrapment material, for example, polymers, capsules, microcapsules and nanocapsules, liposomes, film formers, absorbents such as carbon or zeolites, cyclic oligosaccharides and mixtures thereof, or they may be chemically bonded to substrates, which are adapted to release the fragrance molecule upon application of an external stimulus such as light, enzyme, or the like, and then mixed with the application.

Thus, the invention additionally provides a method of manufacturing a fragrance application, comprising the incorporation of a compound of formula (I) as a fragrance ingredient, either by directly admixing the compound of formula (I) to the application or by admixing a fragrance composition comprising a compound of formula (I), which may then be mixed to a fragrance application, using conventional techniques and methods.

As used herein, "fragrance application" means any product, such as fine perfumery, e.g. perfume and Eau de Toilette; household products, e.g. detergents for dishwasher, surface cleaner; laundry products, e.g. softener, bleach, detergent; body care products, e.g. shampoo, shower gel; and cosmetics, e.g. deodorant, vanishing creme, comprising an odourant. This list of products is given by way of illustration and is not to be regarded as being in any way limiting.

Compounds of formula (I) wherein R^4 and R^5 together with the carbon atom to which they are attached form a carbonyl group (see formula (II) below) may be prepared by the reaction of α-pinene with α,β-unsaturated carboxylic acids or derivatives thereof such as alkenoyl halogenide, e.g. crotonyl chloride, crotonyl bromide and pentenoyl chloride; or alkenoyl anhydride, for example crotonic anhydride, in the presence of a catalytic amount of an acid, such as Lewis acid or Bronsted acid.



(II)

Surprisingly we have found that certain compounds of formula (I) may also be prepared by reacting α-pinene with β,γ-unsaturated carboxylic acids or β-hydroxy carboxylic acids, resulting in a ketone of formula (II) in the presence of a catalytic amount of an acid. It is believed that, due to the acidic conditions, both the β,γ-unsaturated carboxylic acids and the β-hydroxy carboxylic acids will transfer to the corresponding α,β-unsaturated carboxylic acids, which then will react with α-pinene.

The resulting compounds of formula (II) may be alkylated to give further compounds of formula (I). Still further compounds of formula (I) may be prepared by reduction and/or acylation of the carbonyl group at C2 or by Grignard reaction and acylation of the carbonyl group at C2. Still further compounds of formula (I) may be prepared by hydrogenation.

Compounds of formula (I) wherein either R^2 or R^3 is not hydrogen, and R^4 and R^5 together with the carbon atom to which they are attached form a carbonyl group may also be prepared by the reaction of α-pinene with α,β-unsaturated α-alkyl carboxylic acids, e.g. 2-methylcrotonyl chloride, 2-ethylcrotonyl chloride, 2-methylcrotonic anhydride, in the presence of a catalytic amount of an acid.

Optically pure compounds of formula (I) and enantiomer mixtures of a compound of formula (I) enriched in one enantiomer may be synthesised by starting from the optically pure α-pinene or from an enantiomer mixture enriched in either (S)-(+)-α-pinene or (R)-(-)- α-pinene respectively.

The invention is now further described with reference to the following non-limiting examples.

Example1: 5-Isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-one (**1**)

a) A mixture of 30g α-pinene ((1*S*)-(-)/(1*R*)-(+) 90:10, 0.22mol), 67.8g crotonic anhydride (0.44mol, 2 eq.), and 4.95g zinc bromide (0.021mol, 0.1 eq.) was heated at 95°C for 7h. The reaction mixture was then treated with 50ml H_2O and heated 3h at reflux. Extraction with Et_2O, drying of the org. phases with Na_2SO_4 followed by *Vigreux*-distillation and FC (Flash Chromatography) (SiO_2, hexane/Et_2O 95:5) gave 990mg (2%) of compound **1**. The boiling point of the end product is 80°C at 0.07 torr (0.09 mbar).

$[\alpha]_D^{22}$ = –280.5 (c=0.93, EtOH)

Odour description: woody, resinous, fir, fruity raspberry ketone-like, olibanum-like, ciste, ambery

b) According to the procedure described above starting from (-)-α-pinene in the presence of crotonyl chloride at 90°C for 4 hours.

$[\alpha]_D^{22}$ = –785 (c=0.75, EtOH)

Odour description: fruity, woody, piny, ambery

c) According to the procedure describe above starting from (+)-α-pinene in the presence of crotonic anhydride at 95°C for 6h.

$[\alpha]_D^{22}$ = +536.2 (c=1.02, EtOH)

Odour description: grapefruit, red fruit, piny, ambery

^{1}H-NMR (400MHz, $CDCl_3$): δ 5.63-5.59 (br. *m*, H-C(7)), 4.75-4.72 (br. *s*, H_t-CH=), 4.64-4.62 (br. *s*, H_c-CH=), 3.08 (*dd*, J = 6.7, 14.5, H_α-C(3)), 2.82-2.78 (br. *s*, H-C(1)), 2.45-2.31 (*m*, C(6)H_2), 2.27 (*quintet t*, J = 2.0, 7.0, H-C(4)), 2.18 (*dd*, J = 3.3, 12.8, irrad. at 2.80 → *d*, J = 12.8, H_{syn}-C(9)), 1.89 (*dt*, J = 1.6, 14.5, irrad. at 2.80 → *dd*, J = 1.6, 14.0, H_β-C(3)), 1.87 (*dt*, J = 2.6, 12.8, irrad. at 2.80 → *dd*, J = 2.2, 13.0, H_{anti}-C(9)), 1.73 (*s*, *Me*C=CH_2), 1.66 (br. *s*, J = 1.9, MeC(8)), 0.80 (*d*, J = 7.2, MeC(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ212.42 (*s*, CO), 150.75 (*s*, C(5)*C*=), 134.36 (*s*, C(8)), 124.85 (*d*, C(7)), 108.75 (*t*, CH_2=), 53.98 (*d*, C(1)), 40.92 (*t*, C(3)), 39.40 (*d*, C(4)), 39.25 (*t*, C(6)), 39.17 (*s*, C(5)), 31.20 (*t*, C(9)), 21.79 (*q*, *Me*C(8)), 18.42 (*q*, *Me*C=CH_2), 16.59 (*q*, *Me*C(4)).

MS (EI): 204 (34), 189 (8), 171 (4), 161 (11), 147 (19), 134 (30), 133 (50), 119 (99), 105 (78), 97 (93), 93 (100), 91 (87), 77 (49), 69 (28), 41(70).

IR: ν_{max} 2954, 2877, 1718, 1659, 1445, 1376, 1311, 1292, 1267, 1182,1101, 1027, 968, 838, 688 cm^{-1}.

Example 2: 4-Ethyl-5-isopropenyl-8-methylbicyclo[3.3.1]non-7-en-2-one (**2**)

At 30°C, a mixture of 7.35g of 2-pentenoyl chloride (62mmol) and 1.7g of zinc chloride (12mmol, 0.2 eq.) in 85ml ethylene chloride was treated dropwise within 20 min. with a solution of 19.4g of (-)-alpha-pinene (142mmol, 2 eq.) in 20ml ethylene dichloride. The reaction mixture was then stirred at 30°C for 30min., then at 50°C for 2h, and finally at 80°C for 1h. After cooling, the reaction mixture was washed with aq. sat. NaCl soln. and aq. sat. $NaHCO_3$ soln. The aq. phases were extracted with Et_2O, dried (Na_2SO_4), and concentrated. FC (SiO_2, hexane/Et_2O 20:1) of the crude (26 g) gave 1.74 g (13%) of compound **2**. The boiling point of the end product is 95°C at 0.06 torr (0.08 mbar).

^{1}H-NMR (400MHz, $CDCl_3$): δ5.63-5.60 (*tq*, J = 1.5, 3.5, H-C(7)), 4.63 (*quintet*, J = 1.3, H_t-CH=), 4.66-4.65 (br. *s*, H_c-CH=), 2.93 (*ddd*, J = 1.6, 6.3, 14.7, H_α-C(3)), 2.81-2.78 (br. *s*, H-C(1)), 2.44-2.30 (*m*, C(6)H_2), 2.14 (*dt*, J = 1.6, 14.8, H_β-C(3)), 2.09 (*dd*, J = 3.4, 12.6, H_{syn}-C(9)), 1.89 (*dt*, J = 2.7, 12.6, H_{anti}-C(9)), 1.88-1.81 (*m*, H-C(4)), 1.72 (*dd*, J = 0.6, 1.3, *Me*C=CH_2), 1.67 (*td*, J = 1.5, 2.3, MeC(8)), 1.36-1.24 (*sext t*, J = 1.8, 7.7, 13.5, MeC*H*-C(4)), 1.03-1.09 (*dqd*, J = 6.2, 7.3, 13.4, MeC*H*-C(4)), 0.87 (*d*, J = 7.2, *Me*CH_2).

^{13}C-NMR (100MHz, $CDCl_3$): δ212.75 (*s*, CO), 151.13 (*s*, C(5)*C*=), 134.71 (*s*, C(8)), 125.04 (*d*, C(7)), 109.09 (*t*, CH_2=), 53.98 (*d*, C(1)), 47.24 (*d*, C(4)), 40.07 (*s*, C(5)), 39.52 (*t*, C(6)), 36.64 (*t*, C(3)), 32.19 (*t*, C(9)), 22.48 (*t*, CH_2Me), 21.97 (*q*, *Me*C(8)), 18.76 (*q*, *Me*C=CH_2), 12.77 (*q*, *Me*CH_2).

MS (EI): 219 (5), 218 (28), 203 (5), 190 (4), 189 (14), 175 (9), 162 (4), 161 (15), 148 (5), 147 (16), 145 (5), 136 (9), 135 (26), 134 (44), 133 (56), 132 (12), 131 (6), 126 (5), 125 (7), 121 (19), 120 (20), 119 (100), 117 (17), 115 (15), 112 (5), 111 (68), 108 (12), 107

(26), 106 (17), 105 (74), 103 (9), 97 (17), 95 (20), 94 (15), 93 (90), 92 (34), 91 (84), 83 (28), 81 (14), 80 (8), 79 (34), 78 (12), 77 (47), 42 (17), 65 (20), 55 (39), 53 (21), 51 (10), 41 (55), 39 (28), 29 (13), 27 (11).

IR: ν_{max} 2963, 2928, 2876, 1707, 1678, 1638, 1448, 1379, 1225, 1153, 1089, 1062, 1009, 916, 889, 857, 811, 786, 717 cm^{-1}.

$[\alpha]_D^{22}$ = -572.7 (1.07 in EtOH)

Odour description: ambery, woody, spicy

Example 3: (1*S**3*S**4*S**5*R**)-5-Isopropenyl-3,4,8-trimethylbicyclo[3.3.1]non-7-en-2-one (3)

At 0°C, 15.3ml of a soln. of LDA (2M in THF/heptane/ethylbenzene, 31mmol, 2.5 eq.) was treated dropwise with a soln. of 2.5 g of 5-Isopropenyl-4,8-dimethyl-bicyclo[3.3.1]non-7-en-2-one (12mmol) in 25ml THF. The reaction mixture was stirred 1.5h at 0°C, treated with 2.6ml methyl iodide (41.7mmol, 3.4 eq.), stirred at 25°C for 3h, and poured into 1M aq. HCl soln. Extraction with MTBE (2 X 80 ml), washing of the org. phase with H_2O, aq. sat. NaCl soln., drying ($MgSO_4$) gave 3.6 g crude. FC (hexane/MTBE 24:1) gave 0.56g (21%) of compound **3**.The boiling point of the end product is 120°C at 0.08 mbar. R_f (hexane/MTBE 24:1) 0.26.

^{1}H-NMR (400MHz, $CDCl_3$): δ5.54-5.50 (*m*, H-C(7)), 4.78 (*quintet*, J = 1.3, H_t-CH=), 4.72-4.70 (br. *s*, H_c-CH=), 2.82-2.78 (br. *s*, H-C(1)), 2.35-2.22 (*m*, C(6)H_2, H_{syn}-C(9), H-C(3)), 1.84 (*dq (quintet)*, J = 7.3, H-C(4)), 1.79 (*td*, J = 1.6, 2.3, MeC(8)), 1.72 (*dd*, J = 0.9, 1.6, *Me*C=CH_2), 1.70 (*dd*, J = 2.3, 13.0, H_{anti}-C(9)), 1.20 (*d*, J = 7.5, Me-C(3)), 0.86 (*d*, J = 7.2, Me-C(4)).

^{1}H-NMR (400MHz, C_6D_6): δ5.24-5.20 (*m*, H-C(7)), 4.78 (*quintet*, J = 1.4, H_t-CH=), 4.63-4.60 (br. *s*, H_c-CH=), 2.71-2.67 (br. *s*, H-C(1)), 2.10-2.03 (*m*, H_β-C(6)), 2.07 (*dq (quintet)*, J = 7.5, H-C(3)), 1.91 (*ddd*, J = 1.9, 2.8, 13.0, H_{syn}-C(9)), 1.93-1.85 (*ddt*, J = 1.8, 4.6, 13.0, H_α-C(6)), 1.76 (*td*, J = 1.6, 2.3, MeC(8)), 1.55 (*dq (quintet)*, J = 7.3, H-C(4)), 1.54 (*dd*, J = 0.9, 1.6, *Me*C=CH_2), 1.35 (*dd*, J = 2.9, 13.0, H_{anti}-C(9)), 1.12 (*d*, J = 7.3, Me-C(3)), 0.69 (*d*, J = 7.2, Me-C(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ212.75 (*s*, CO), 151.01 (*s*, C(5)*C*=), 132.72 (*s*, C(8)), 124.48 (*d*, C(7)), 109.60 (*t*, CH_2=), 51.98 (*d*, C(1)), 48.25 (br. *d*, C(3)), 41.15 (br. *d*,

C(4)), 39.35 (*t*, C(6)), 39.33 (*s*, C(5)), 29.99 (*t*, C(9)), 21.58 (*q*), 20.12 (*q*), 19.50 (br. *q*), 18.22 (*q*).

^{13}C-NMR (100MHz, C_6D_6): δ210.1 (*s*, CO), 151.0 (*s*, C(5)*C*=), 133.3 (*s*, C(8)), 123.9 (*d*, C(7)), 110.1 (*t*, CH_2=), 51.8 (*d*, C(1)), 47.4 (br. *d*, C(3)), 40.6 (br. *d*, C(4)), 39.7 (*s*, C(5)), 39.4 (*t*, C(6)), 30.2 (*t*, C(9)), 21.8 (*q*, Me-C(8)), 20.6 (*q*), MeC=CH_2), 17.9 (br. *q*, Me-C(3)), 17.6 (*q*, Me-C(4)).

MS (EI): 218 (27), 203 (8), 190 (8), 185 (3), 175 (8), 161 (11), 147 (19), 133 (66), 119 (100), 111 (47), 107 (47), 105 (72), 93 (72), 91 (76), 83 (57), 77 (43), 65 (18), 55 (48), 41 (62).

IR: ν_{max} 2969, 2934, 1708, 1636, 1448, 1376, 1233, 1155, 1092, 1061, 1040, 994, 955, 919, 890, 814, 781, 734, 649 cm^{-1}.

$[a]_D^{22}$ = -655.3 (c=0.99, EtOH)

Odour description: woody, green, floral, rosy, ambery

Example 4: 5-Isopropenyl-3,3,4,8-tetramethylbicyclo[3.3.1]non-7-en-2-one (**4**)

At 55°C, a mixture of 9.9g KOH (176 mmol, 15 eq.) in 40ml DMSO was treated dropwise with a soln. of 2.4g of of 5-isopropenyl-4,8-dimethyl-bicyclo[3.3.1]non-7-en-2-one (11.7mmol) in 3.7ml methyliodide (59mmol, 5 eq.). The reaction mixture was stirred 1.5h at 60°C, treated with 2.0ml methyl iodide (32mmol, 2.7 eq.), stirred at 60°C for 1.5h, treated with 1.7ml methyl iodide (27mmol, 2.3 eq.), stirred at 60°C for 1.5h, cooled, and poured into 200ml of 2M aq. HCl soln. Extraction with hexane (2 X 100ml), washing of the org. phase with H_2O, aq. sat. NaCl soln., drying ($MgSO_4$) gave 2.6g crude. FC (hexane/MTBE 15:1) gave 0.7g (26%) of compound **4**. The boiling point of the end product is 120°C at 0.08 mbar. R_f (hexane/MTBE 15:1) 0.27.

^{1}H-NMR (400MHz, $CDCl_3$): δ5.55-5.51 (*m*, H-C(7)), 4.83 (*quintet*, J = 1.4, H_t-CH=), 4.75-4.73 (br. *s*, H_c-CH=), 2.86-2.83 (*m*, H-C(1)), 2.43-2.35 (*m*, H-C(6)), 2.33-2.25 (*m*, H-C(6)), 2.28 (*ddd*, J = 1.6, 3.0, 13.0, H_{anti}-C(9)), 1.96 (*qd*, J = 1.0, 7.4, H-C(4)), 1.80 (*dd*, J = 0.5, 1.3, *Me*C=CH_2),)), 1.70 (*dd*, J = 1.1, 13.0, H_{syn}-C(9)), 1.70 (*q*, J ≈ 1.8, MeC(8)), 1.21 (*s*, Me), 1.07 (*s*, Me), 0.85 (*d*, J = 7.5, MeC(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ214.58 (*s*, CO), 151.65 (*s*, C(5)*C*=), 133.10 (*s*, C(8)), 124.94 (*d*, C(7)), 109.91 (*t*, CH_2=), 52.58 (*d*, C(1)), 47.15 (*s*, C(3)), 45.15 (*d*, C(4)), 40.64 (*s*, C(5)), 40.49 (*t*, C(6)), 31.33 (*q*), 30.55 (*t*, C(9)), 25.21 (*q*), 22.18 (*q*), 21.44 (*q*), 13.95 (*q*).

MS (EI): 218 (27), 203 (8), 190 (8), 185 (3), 175 (8), 161 (11), 147 (19), 133 (66), 119 (100), 111 (47), 107 (47), 105 (72), 93 (72), 91 (76), 83 (57), 77 (43), 65 (18), 55 (48), 41 (62).

IR: ν_{max} 2969, 2934, 1708, 1636, 1448, 1376, 1233, 1155, 1092, 1061, 1040, 994, 955, 919, 890, 814, 781, 734, 649 cm^{-1}.

Odour description: woody, ambery

Example 5: (1*S**4*S**5*R**)-5-Isopropenyl-8,8-dimethoxy-2,6-dimethylbicyclo[3.3.1]non-2-ene (5)

A soln. of 1.5g of 5-isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-one (7.3mmol), 1.4g para-toluenesulfonic acid mono hydrate (7.4mmol 1 eq.), and 0.78g trimethyl-orthoformate (7.4mmol, 1 eq.) in 50ml methanol was heated at 60°C for 66h. The reaction mixture was then cooled and poured into aq. sat. $NaHCO_3$ soln. (20ml). Extraction with MTBE (2 X 80 ml) followed by washing of the aq. phases with H_2O and aq. sat. NaCl soln., drying of org. phases ($MgSO_4$) led to 1.8g of crude product. FC (SiO_2, Hexane/MTBE 30:1) gave 1.7 g (92%) of compound **5** as colorless liquid. The boiling point of the end product is 130°C at 0.08 mbar. R_f (hexane/MTBE 8:1) 0.57.

^{1}H-NMR (400MHz, $CDCl_3$): δ5.48 (*tq*, J = 1.4, 3.7, H-C(7)), 4.63 (*quintet*, J = 1.4, H_c-CH=), 4.61-4.60 (br. *s*, H_c-CH=), 3.20 (*s*, OMe), 3.17 (*s*, OMe), 2.49-2.45 (*m*, irrad. at 1.43 → changes, H-C(1)), 2.17-2.02 (*m*, C(6)H_2), 1.97 (*dd*, J = 3.0, 12.4, irrad. at 1.43 → br. *d*, J ≈ 4.0, H_{syn}-C(9)), 1.88 (*dd*, J ≈ 6.2, 14.4, H_α-C(3)), 1.90-1.81 (*m*, irrad. at 1.43 → changes, H-C(4)), 1.79 (*td*, J = 1.7, 2.1, MeC(8)), 1.66 (*dd*, J = 0.6, 1.4, *Me*C=CH_2), 1.69-1.61 (*m*, irrad. at 2.47 → changes, H_β-C(3)), 1.43 (*ddd*, J = 1.6, 3.5, 12.5, irrad. at 2.47 → *dd*, J = 1.4, 12.6, H_{anti}-C(9)), 0.88 (*d*, J = 7.7, MeC(4)).

^{1}H-NMR (400MHz, C_6D_6): δ5.49-5.45 (*m*, H-C(7)), 4.77-4.73 (*m*, CH_2=), 3.05 (*s*, OMe), 3.03 (*s*, OMe), 2.49-2.44 (*m*, H-C(1)), 2.12-2.05 (*m*, H-C(6)), 2.05 (*dd*, J = 2.8, 12.3,

H_{syn}-C(9)), 1.96 (*td*, J = 1.7, 2.1, MeC(8)), 1.99-1.91 (*m*, H-C(6)), 1.93 (*dd*, J = 6.2, 13.5, H_{α}-C(3)), 1.71 (*quintet t*, J = 1.7, 7.2, H-C(4)), 1.63 (*dt*, J = 1.9, 13.5, H_{β}-C(3)),1.61 (*dd*, J = 0.6, 1.2, *Me*C=CH_2), 1.48 (*ddd*, J = 1.8, 3.5, 12.4, H_{anti}-C(9)), 1.06 (*d*, J = 7.3, MeC(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ 152.59 (*s*, C(5)*C*=), 135.79 (*s*, C(8)), 124.07 (*d*, C(7)), 107.32 (*t*, CH_2=), 102.98 (*s*, C(2)), 47.59 (*q*, OMe), 47.47 (*q*, OMe), 40.59 (*d*), 40.14 (*t*, C(6)), 39.12 (*s*, C(5)), 37.05 (*d*), 32.53 (*t*, C(9)), 27.90 (*t*, C(3)), 24.45 (*q*), 18.33 (*q*), 17.41 (*q*).

^{13}C-NMR (100MHz, C_6D_6): δ 152.71 (*s*, C(5)*C*=), 136.37 (*s*, C(8)), 124.13 (*d*, C(7)), 107.78 (*t*, CH_2=), 103.25 (*s*, C(2)), 47.46 (*q*, OMe), 46.38 (*q*, OMe), 40.90 (*d*), 40.61 (*t*, C(6)), 39.65 (*s*, C(5)), 37.47 (*d*), 33.36 (*t*, C(9)), 27.30 (*t*, C(3)), 24.97 (*q*), 18.57 (*q*), 18.02 (*q*).

MS (EI): 250 (0.2), 218 (31), 203 (19), 187 (5), 171 (12), 137 (57), 115 (100), 91 (35), 77 (23), 69 (15), 55 (16), 41 (35).

IR: ν_{max} 2945, 2829, 1638, 1451, 1366, 1308, 1194, 1160, 1130, 1110, 1086, 1051, 1018, 972, 953, 922, 886, 846, 799, 772 cm^{-1}.

$[\alpha]_D^{22}$ = -150.1 (c=1.00, EtOH)

Odour description: ambery, woody, fruity, sweet

Example 6:(1*S**4*S**5*R**)- 4,8-Dimethyl-5-isopropenylspiro[bicyclo[3.3.1]nonane-2,2'-[1,3]dioxolane] (**6**)

A soln. of 2.0g of 5-isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-one (9.8mmol) in 100ml cyclohexane was treated with 1.8g ethyleneglycol (2.9mmol, 3.0 eq.) and 0.2g para-toluenesulfonic acid mono hydrate (1.0mmol 0.1 eq.). The soln. obtained was heated at reflux for 3h (Dean-Stark apparatus), cooled and poured into aq. sat. $NaHCO_3$ soln. (100ml). Extraction with MTBE (2 x 80ml) followed by washing of the aq. phases with H_2O (100ml) and aq. sat. NaCl soln. (150ml), drying of org. phases over $MgSO_4$ led to 2.6g of crude product. FC (SiO_2, hexane/MTBE 19:1) gave 0.76g (31%) of compound **6** as colorless liquid. The boiling point of the end product is 130°C at 0.09 mbar. R_f (hexane/MTBE 19:1) 0.47.

^{1}H-NMR (400MHz, $CDCl_3$): δ5.49 (*tq*, J = 1.4, 3.5, H-C(7)), 4.64 (*quintet*, J = 1.4, H_t-CH=), 4.62-4.60 (br. *s*, H_c-CH=), 4.03-3.88 (*m*, OCH_2CH_2O), 2.21-2.18 (br. *s*, H-C(1)), 2.17 (*dd*, J = 6.2, 13.8, H_α-C(3)), 2.14-2.09 (*m*, C(6)H_2), 2.09 (*dd*, J = 2.9, ,12.9, H_{syn}-C(9)), 1.92 (*quintet t*, J = 1.7, 7.2, H-C(4)), 1.79 (*td*, J = 1.5, 2.2, MeC(8)), 1.66 (*dd*, J = 0.6, 1.3, *Me*C=CH_2), 1.52 (*ddd*, J = 1.9, 3.4, 12.6, H_{anti}-C(9)), 1.36 (*dt*, J = 1.8, 13.9, H_β-C(3)), 0.89 (*d*, J = 7.2, MeC(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ152.43 (*s*, C(5)*C*=), 135.84 (*s*, C(8)), 123.96 (*d*, C(7)), 111.52 (*s*, C(2)), 107.53 (*t*, CH_2=), 64.27 (*t*, OCH_2), 63.46 (*t*, OCH_2), 43.56 (*d*), 39.89 (*t*, C(6)), 38.92 (*s*, C(5)), 37.34 (*d*), 34.16 (*t*, C(9)), 28.70 (*t*, C(3)), 23.97 (*q*), 18.32 (*q*), 16.88 (*q*).

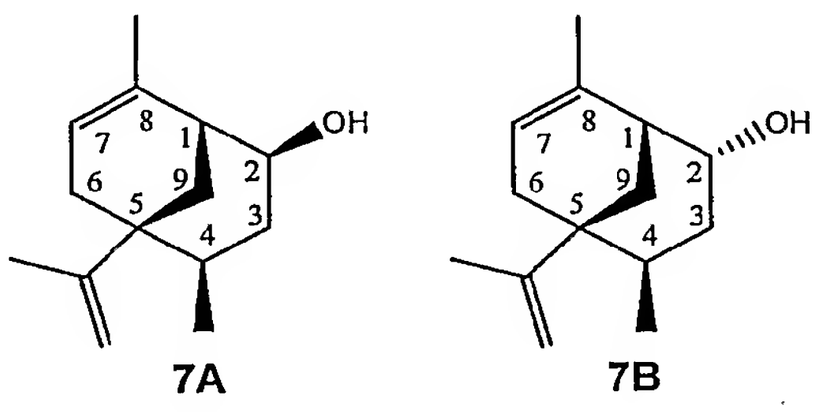
MS (EI): 248 (1), 233 (0.2), 203 (0.3), 147 (2), 133 (3), 119 (5), 113 (100), 105 (6), 91 (9), 86 (4), 77 (5), 69 (9), 41 (9).

IR: ν_{max} 2962, 2885, 1638, 1450, 1368, 1308, 1162, 1129, 1110, 1083, 1063, 1042, 1020, 975, 953, 925, 887, 845, 831, 801 cm^{-1}.

$[\alpha]_D^{22}$ = -142.8 (c=0.51, EtOH)

Odour description: fruity, spicy, woody

Example 7: 5-Isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-ol (**7A** and **7B**)



7A **7B**

At 5°C, a soln. of 1g of 5-isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-one (4.9mmol) in 5ml ethanol was treated with 0.37g $NaBH_4$ (9.8mmol, 2 eq.). The reaction mixture was then stirred 2h at 25°C, poured into 1N aq. HCl soln., and extracted with Et_2O. The org. phase was washed with aq. sat. NaCl soln., dried, and concentrated. FC

(hexane/Et_2O 9:1 to 9:2) of the crude (1g, **7A/7B** 30:70) gave 0.1 g **7A** (10%), 0.2 g **7A/7B** (1:1, 20%), and 0.4 g **7B** (40%).

(1*S**2*R**4*S**5*R**)-5-Isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-ol (**7A** (exo))

Boiling point: 100°C at 0.06 torr (0.08mbar).

^{1}H-NMR (400MHz, $CDCl_3$): δ5.44 (*tq*, J = 1.4, 3.5, H-C(7)), 4.67-4.64 (*m*, C=CH_2), 3.90 (*dt*, J = 2.8, 2.9, H-C(2)), 2.29-2.25 (*m*, H-C(1)), 2.20 (*dd*, J = 3.0, 12.6, H_{syn}-C(9)), 2.10-2.05 (*m*, C(6)H_2), 2.02 (*ddd*, J = 3.7, 6.2, 14.9, H_α-C(3)), 1.82-1.75 (*m*, H-C(4)), 1.69 (*td*, J = 1.6, 2.1, MeC(8)), 1.66 (*dd*, J = 0.6, 1.1, *Me*C=CH_2), 1.45 (*ddt*, J = 1.6, 1.8, 14.8, H_β-C(3)), 1.37 (*ddd*, J = 1.2, 1.7, 12.6, H_{anti}-C(9)), 0.98 (*d*, J = 7.3, MeC(4)).
^{13}C-NMR (100MHz, $CDCl_3$): δ152.93 (*s*, C(5)*C*=), 135.27 (*s*, C(8)), 123.66 (*d*, C(7)), 107.21 (*t*, CH_2=), 68.41 (*d*, C(2)), 43.39 (*d*), 39.36 (*t*, C(6)), 39.18 (*s*, C(5)), 35.96 (*d*), 32.99 (*t*, C(9)), 24.12 (*t*, C(3)), 22.26 (*q*, *Me*C(8)), 18.87 (*q*, *Me*C=CH_2), 17.91 (*q*, *Me*C(4)).
MS (EI): 206 (17), 188 (44), 173 (32), 159 (14), 147 (19), 145 (26), 133 (58), 119 (66), 107 (71), 105 (77), 93 (100), 77 (50), 71 (24), 55 (36), 41 (70).
$[\alpha]_D^{22}$ = -141.4 (c=0.89, EtOH)

Odour description: floral, agrestic, rosy, green

(1*S**2*S**4*S**5*R**)-5-Isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-ol (**7B**(endo))

Boiling point: 80°C at 0.05 torr (0.07mbar).

^{1}H-NMR (400MHz, $CDCl_3$): δ5.60 (*tq*, J = 1.5, 3.5, H-C(7)), 4.63 (*quintet*, J = 1.4, H_t-CH=), 4.58-4.56 (br. *s*, H_c-CH=), 4.03 (*dt*, J = 4.4, 11.5, irrad. at 2.48 → *dd*, J ≈ 4.4, 11.2, H-C(2)), 2.50-2.45 (*m*, irrad. at 4.03 → changes, H-C(1)), 2.12-2.00 (br. *s*, C(6)H_2), 1.89 (br. *quintet t*, J = 1.7, 7.1, H-C(4)),1.86-1.76 (*m*, irrad. at 4.03 → changes, irrad. at 2.48 → changes, H_{syn}-C(9), H_α-C(3)), 1.81 (*td*, J = 1.6, 2.2, MeC(8)), 1.64 (br. *d*, J = 0.8, *Me*C=CH_2), 1.57 (*ddd*, J = 1.8, 3.7, 12.8, irrad. at 2.48 → *dd*, J ≈ 2.0, 12.8, H_{anti}-C(9)), 1.55 (*dddd*, J = 1.4, 1.8, 4.4, 12.4, irrad. at 4.03 → *dt*, J ≈ 1.9, 11.6, irrad. at 2.48 → *dd*, J = 2.0, 4.4, 12.4, H_β-C(3)), 1.33-1.21 (br. *s*, OH), 0.80 (*d*, J = 7.2, MeC(4)).

^{1}H-NMR (400MHz, C_6D_6): δ5.52 (*tq*, J = 1.5, 3.4, H-C(7)), 4.68 (*quintet*, J = 1.4, H_c-CH=), 4.63-4.61 (br. *s*, H_c-CH=), 3.73 (*dt*, J = 4.4, 11.6, H-C(2)), 2.29-2.25 (*m*, H-C(1)), 2.03-1.95 (*m*, H-C(6)), 1.91 (*td*, J = 1.6, 2.1, MeC(8)), 1.88-1.80 (*m*, H-C(6)), 1.77 (*td*, J = 5.3, 12.2, H_α-C(3)), 1.61 (br. *quintet t*, J = 1.8, 7.2, H-C(4)), 1.62-1.57 (*m*, H_{syn}-C(9)), 1.52 (*dd*, J = 0.6, 1.3, *Me*C=CH_2), 1.49 (*ddd*, J = 1.8, 3.7, 12.7 H_{anti}-C(9)), 1.30 (*dddd*, J = 1.3, 2.0, 4.4, 12.6, H_β-C(3)), 0.71 (*d*, J = 7.2, MeC(4)), 0.66-0.57 (br. *s*, OH).

^{13}C-NMR (100MHz, $CDCl_3$): δ152.26 (*s*, C(5)*C*=), 133.63 (*s*, C(8)), 124.24 (*d*, C(7)), 107.48 (*t*, CH_2=), 69.53 (*d*, C(2)), 42.84 (*d*), 39.94 (*t*, C(6)), 38.64 (*s*, C(5)), 37.23 (*d*), 34.61 (*t*, C(9)), 29.57 (*t*, C(3)), 25.05 (*q*, *Me*C(8)), 18.26 (*q*, *Me*C=CH_2), 16.15 (*q*, *Me*C(4)).

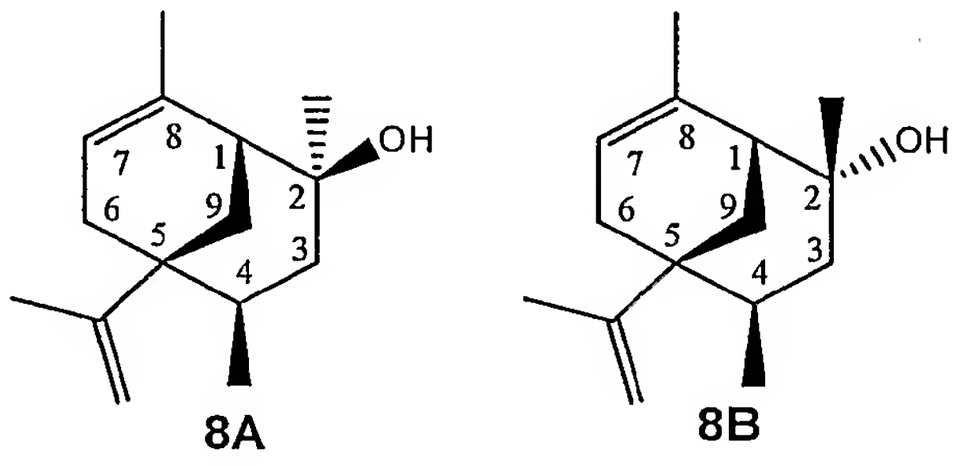
MS (EI): 206 (17), 188 (44), 173 (32), 159 (14), 147 (19), 145 (26), 133 (58), 119 (66), 107 (71), 105 (77), 93 (100), 77 (50), 71 (24), 55 (36), 41 (70).

IR: ν_{max} 3282, 2966, 2933, 2880, 1637, 1443, 1375, 1355, 1329, 1296, 1250, 1162, 1079, 1047, 1029, 998, 887, 821, 792, 632 cm^{-1}.

$[\alpha]_D^{22}$ = -226.0 (c=0.98, EtOH)

Odour description: floral, isononanol-like, grapefruit

Example 8: 5-Isopropenyl-2,4,8-trimethylbicyclo[3.3.1]non-7-en-2-ol (8A and 8B)



8A 8B

At 5°C, a soln. of 1g of 5-isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-one (4.9mmol) in 15ml THF was treated dropwise with 21ml 1.4M MeLi in Et_2O (29.4mmol, 6 eq.). The reaction mixture was stirred 5h at 5°C, warmed to 25°C overnight, poured into aq. sat. NH_4Cl soln., and extracted with Et_2O. The org. phase was washed with aq. sat. NaCl soln., dried, and concentrated. FC (SiO_2, hexane/Et_2O 9:1) of the crude (1.2g,

starting material/OH exo/OH endo 17:65:18) gave 0.2g of starting material (20%), 0.5 g **8A** (46%), 0.25 g **8A/8B** (1:1, 23%), and 0.1 g **8B** (9%).

(1*S**2*R**4*S**5*R**)-5-Isopropenyl-2,4,8-trimethylbicyclo[3.3.1]non-7-en-2-ol (**8A**(exo))

Boiling point: 80°C at 0.07 torr (0.09mbar).

^{1}H-NMR (400MHz, $CDCl_3$): δ5.44 (*tq*, J = 1.5, 3.7, H-C(7)), 4.66-4.64 (br. *s*, H_c-CH=), 4.63 (*quintet*, J = 1.4, H_t-CH=), 2.26 (*dd*, J = 3.1, 12.5, H_{syn}-C(9)), 2.10-2.05 (*m*, C(6)H_2, H-C(1)), 1.92 (*dd*, J = 6.1, 14.4, H_α-C(3)), 1.81 (*quintet t*, J = 1.5, 7.2, H-C(4)),1.77 (*td*, J = 1.5, 2.2, MeC(8)), 1.67 (*dd*, J = 0.6, 1.3, *Me*C=CH_2), 1.38 (*ddd*, J = 1.5, 3.0, 12.5, H_{anti}-C(9)), 1.31 (*dt*, J = 1.6, 14.4, H_β-C(3)), 1.27-1.21 (br. *s*, OH), 1.18 (*s*, MeC(2)), 0.98 (*d*, J = 7.3, MeC(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ152.70 (*s*, C(5)C=), 135.83 (*s*, C(8)), 124.48 (*d*, C(7)), 107.11 (*t*, CH_2=), 73.24 (*s*, C(2)), 47.84 (*d*, C(1)), 39.91 (*t*, C(6)), 38.86 (*s*, C(5)), 38.49 (*t*), 36.85 (*d*, C(4)), 31.31 (*q*, *Me*C(2)), 26.92 (*t*), 24.57 (*q*, *Me*C(8)), 18.06, 18.03 (2*q*, *Me*C=CH_2, *Me*C(4)).

MS (EI): 220 (6), 202 (22), 187 (18), 162 (48), 147 (21), 135 (56), 119 (55), 107 (66), 93 (74), 85 (100), 77 (39), 67 (26), 55 (28), 43 (81).

IR: ν_{max} 3417, 2968, 2928, 2833, 1640, 1446, 1372, 1329, 1302, 1210, 1151, 1121, 1104, 1033, 942, 926, 886, 832, 800, 781 cm^{-1}.

Odour description: fruity, agrestic, rosy, earthy

(1*S**2*S**4*S**5*R**)-5-Isopropenyl-2,4,8-trimethylbicyclo[3.3.1]non-7-en-2-ol (**8B**(endo))

Boiling point: 60°C at 0.06 torr (0.08mbar).

^{1}H-NMR (400MHz, $CDCl_3$): δ5.56 (*tq*, J = 1.6, 3.5, H-C(7)), 4.62 (*quintet*, J = 1.4, H_t-CH=), 4.60-4.58 (br. *s*, H_c-CH=), 2.18-2.14 (*m*, H-C(1)), 2.13-2.08 (*m*, C(6)H_2), 1.97 (*dd*, J = 6.3, 13.1, H_α-C(3)), 1.90 (*quintet t*, J = 1.5, 7.2, H-C(4)), 1.86 (*dd*, J = 3.0, 13.1, H_{syn}-C(9)), 1.84 (*td*, J = 1.5, 2.2, MeC(8)), 1.54 (*ddd*, J = 1.8, 3.5, 13.1, H_{anti}-C(9)), 1.42 (*dt*, J = 1.4, 13.0, H_β-C(3)), 1.41-1.39 (br. *s*, *Me*C=CH_2), 1.32-1.22 (br. *s*, OH), 1.26 (*s*, MeC(2)), 0.83 (*d*, J = 7.5, MeC(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ152.13 (*s*, C(5)*C*=), 135.70 (*s*, C(8)), 124.14 (*d*, C(7)), 107.24 (*t*, CH_2=), 73.32 (*s*, C(2)), 47.42 (*d*, C(1)), 40.90, 40.27 (2*t*, C(3), C(6)), 38.71 (*s*, C(5)), 37.23 (*d*, C(4)), 29.24 (*t*), 29.02 (*q*, *Me*C(2)); 25.46 (*q*, *Me*C(8)), 18.18, 17.49 (2*q*, *Me*C=CH_2, *Me*C(4)).

MS (EI): 220 (4), 202 (24), 187 (16), 162 (46), 147 (22), 135 (56), 119 (55), 107 (66), 93 (74), 85 (100), 77 (39), 67 (26), 55 (28), 43 (81).

IR: ν_{max} 3452, 2924, 2881, 1638, 1448, 1376, 1289, 1258, 1160, 1140, 1109, 1061, 1019, 943, 931, 907, 887, 829, 800, 656 cm^{-1}.

Odour description: fruity, rosy

Example 9: 5-Isopropyl-4,8-dimethylbicyclo[3.3.1]nonan-2-one (**9**)

At 25°C, a mixture of 1 g 5-isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-one (4.9mmol) and 50mg 10% Pd/C in 10ml MeOH was stirred under 10bar of H_2 for 5h. Filtration (Celite®), concentration, and FC (SiO_2, hexane/Et_2O 100:7) gave 0.22g (22%) of compound **9**. The boiling point of the end product is 75°C at 0.07 torr (0.09mbar).

^{1}H-NMR (400MHz, $CDCl_3$): δ2.69 (*dd*, J = 8.2, 17.4, H_α-C(3)), 2.38-2.31 (br. *s*, H-C(1)), 2.20 (br. d, J = 17.1, H_β-C(3)), 2.23-2.12 (*m*, 1H), 1.79-1.38 (*m*, 8H), 0.93 (*d*, J = 7.1, Me), 0.88 (*d*, J = 6.8, Me), 0.84 (*d*, J = 6.2, Me), 0.82 (*d*, J = 6.5, Me).

^{1}H-NMR (400MHz, C_6D_6): δ2.39 (*dd*, J = 8.1, 17.2, H_α-C(3)), 2.31-2.26 (*m*, H-C(1)), 2.12 (br. *d*, J = 17.3, H_β-C(3)), 1.73 (br. *quintet*, J = 7.1, H-C(4)), 1.53-1.41 (*m*, H_{anti}-C(9), H-C(7)), 1.40-1.30 (*m*, H-C(6), H-C(8), C*H*Me_2), 1.29 (*dt*, J = 2.3, 13.5, H_{anti}-C(9)), 1.23-1.10 (*m*, H-C(7), H-C(6)), 0.62 (*d*, J = 6.7, MeC(8)), 0.69 (*d*, J = 6.8, *Me*CHMe), 0.68 (*d*, J = 7.2, MeC(4)), 0.62 (*d*, J = 6.9, *Me*CHMe).

^{13}C-NMR (100MHz, $CDCl_3$): δ214.61 (*s*, CO), 52.70 (*d*), 49.67 (*t*), 37.65 (*d*), 35.51 (*s*), 34.33 (*d*), 33.36 (*t*), 32.98 (*d*), 29.93 (*t*), 28.19 (*t*), 19.86 (*q*), 18.34 (*q*), 17.11 (*q*), 15.84 (*q*).

^{13}C-NMR (100MHz, C_6D_6): δ210.00 (*s*, CO), 52.88 (*d*, C(1)), 49.86 (*t*, C(3)), 37.68 (*d*, C(4)), 35.72 (*s*, C(5)), 34.50 (*d*, C(8)), 33.51 (*t*, C(9)), 33.17 (*d*, CHMe_2), 30.25 (*t*, C(7)), 28.44 (*t*, C(6)), 20.23 (*q*, Me-C(8)), 18.38 (*q*, Me-C(4)), 17.28, 16.03 (2*q*, Me_2C).

MS (EI): 208 (22), 193 (7), 190 (3), 165 (36), 147 (14), 137 (58), 123 (24), 109 (15), 95 (84), 81 (100), 67 (30), 55 (36), 41 (45).

$[a]_D^{22}$ = -108.8 (c=1.06, EtOH)

Odour description: fruity, agrestic, rosy, woody

Example 10: (1*S**5*R**)-5-Isopropenyl-8-methylbicyclo[3.3.1]non-7-en-2-one (**10**)

A mixture of 20.0 g acryloyl chloride (0.22 mol) and 3.01 g zinc chloride (0.02 mol, 0.1 eq.) in 150 ml ethylene chloride was treated with a soln. of 350 ml α-pinene ((1*S*)-(-)/(1*R*)-(+) 90:10, 2.20 mol, 10 eq.) in 250 ml ethylene chloride and the resulting mixture was stirred 1 h at 25°C and 4 h at 50°C. After cooling, the reaction mixture was washed with aq. sat. NaCl soln. and aq. sat. $NaHCO_3$ soln. The aq. phases were extracted with Et_2O, dried (Na_2SO_4), and concentrated. The crude product(48 g) was filtered (SiO_2, hexane/Et_2O 200:6→200:10) and the residue (1.42 g) treated with 300 mg $LiOH{\cdot}H_2O$ in 15 ml MeOH at 25°C for 7h. The resulting mixture was poured into aq. sat. NaCl soln. , extracted with hexane and the org. phases dried with Na_2SO_4. FC (SiO_2, hexane/Et_2O 30:1) gave 347 mg (0.8%) of compound **10**. Boiling point: 80°C at 0.07 torr (0.09mbar).

^{1}H-NMR (400MHz, $CDCl_3$): δ 5.65 (*tq*, J = 1.5, 3.3, H-C(7)), 4.5-4.743 (br. *s*, H_c-CH=), 4.72 (*quintet*, J = 1.4, H_t-CH=), 2.85 (br. *t*, J = 3.1, H-C(1)), 2.79 (*ddd*, J = 6.8, 13.7, 15.4, H_α-C(3)), 2.375 (br. *d*, J = 18.8, H-C(6)), 2.295 (*dddd*, J = 1.9, 3.9, 5.8, 18.9, H-C(6)), 2.12 (*dddd*, J = 1.3, 2.2, 5.9, 15.3, H_β-C(3)), 2.13-2.06 (*m*, H_α-C(4)), 2.03-2.00 (br. *s*, C(9)H_2), 1.78 (*dd*, J = 0.7, 1.3, *Me*C=CH_2), 1.73 (dddd, J = 1.5, 6.0, 13.4, H-C_β (4)), 1.67 (*dt*, J = 1.6, 2.2, MeC(8)).

^{13}C-NMR (100MHz, $CDCl_3$): δ 212.05 (*s*, CO), 152.28 (*s*, C(5)*C*=), 133.76 (*s*, C(8)), 125.20 (*d*, C(7)), 108.06 (*t*, CH_2=), 53.65 (*d*, C(1)), 38.13 (*t*), 36.68 (*t*), 36.00 (*s*, C(5)), 35.64 (*t*), 34.25 (*t*), 21.99 (*q*, *Me*C(8)), 19.06 (*q*, *Me*C=CH_2).

MS (EI): 190 (16), 175 (5), 162 (1), 157 (4), 147 (9), 133 (27), 119 (28), 105 (58), 98 (21), 93 (100), 91 (65), 83 (95), 77 (37), 65 (17), 55 (20), 41(42).

IR: ν_{max} 2929, 1737, 1712, 1637, 1443, 1379, 1241, 1151, 1119, 1058, 993, 890, 789 cm^{-1}.

$[a]_D^{22}$ = -55.0 (c=0.79, EtOH)

Odour description: woody (pine, cedarwood), ambery, sweet

Example 11: (1*S**3R*4*S**5*R**)-5-Isopropenyl-3,4,8-trimethylbicyclo[3.3.1]non-7-en-2-one (**11**)

Method a) A mixture of 11.81 g 2-methyl-but-2-enoyl chloride (0.10 mol) and 1.36 g zinc chloride (0.01 mol, 0.1 eq.) in 100 ml ethylene chloride was treated with a soln. of 136 g α-pinene ((1*S*)-(-)/(1*R*)-(+) 90:10, 1 mol, 10 eq.) in 150 ml ethylene chloride and the resulting mixture was stirred 45 min. at 25°C, 2.5 h at 50°C, and 1h at 80°. After cooling, the reaction mixture was washed with aq. sat. NaCl soln. and aq. sat. $NaHCO_3$ soln. The aq. phases were extracted with Et_2O, dried (Na_2SO_4), and concentrated. The crude product (48 g) filtered (SiO_2, hexane/Et_2O 200:6→200:13) and the residue (5.1 g) treated with 1g $LiOH{\cdot}H_2O$ in 75 ml MeOH at 25°C for 48h. The resulting mixture was poured into aq. sat. NaCl soln. and extracted with hexane. The combined org. phases were dried (Na_2SO_4), concentrated and purified by FC (SiO_2, hexane/Et_2O 100:3) gave 1.6 g (7.1%) of compound **11**.

Method b) 15 ml of a soln. of 0.116 M of EtONa in EtOH were treated with 1.5 g of 5-isopropenyl-3,4,8-trimethylbicyclo[3.3.1]non-7-en-2-one and heated 4 h at reflux. The resulting mixture was poured into 50 ml 2M aq. HCl and extracted with 2X50 ml MTBE. The org. phases were washed with 50 ml H_2O, 50 ml aq. sat. NaCl soln., and dried. FC (SiO_2, hexane/MTBE 20:1) gave 0.75 g (50%) of compound **11**. Boiling point: 80°C at 0.08 mbar.

^{1}H-NMR (400MHz, $CDCl_3$): δ5.61 (*tq*, J = 1.5, 3.2, H-C(7)), 4.73 (*quintet*, J = 1.3, H_t-CH=), 4.64-4.62 (br. *s*, H_c-CH=), 3.26 (*qd*, J = 5.8, 6.7, H-C(3)), 2.83 (br. *t*, J = 3.1, H-C(1)), 2.45-2.33 (*m*, C(6)H_2), 2.13 (*qdd*, J = 2.5, 5.6, 7.0, H-C(4)), 2.11 (*dd*, J = 3.4, 12.6, H_{syn}-C(9)), 1.85 (*dt*, J = 2.7, 12.6, H_{anti}-C(9)), 1.72 (*dd*, J = 0.8, 1.2, *Me*C=CH_2), 1.66 (*dt*, J = 1.6, 2.3, MeC(8)), 0.93 (*d*, J = 6.7, MeC(3)), 0.63 (*d*, J = 7.1, MeC(4)).
^{13}C-NMR (100MHz, $CDCl_3$): δ214.66 (*s*, CO), 151.19 (*s*, C(5)*C*=), 135.89 (*s*, C(8)), 124.96 (*d*, C(7)), 108.94 (*t*, CH_2=), 54.02 (*d*, C(1)), 46.01 (*t*, C(3)), 40.96 (*s*, C(5)), 39.47 (*t*, C(6)), 39.30 (*d*, C(4)), 32.16 (*t*, C(9)), 22.21 (*q*, *Me*C(8)), 18.63 (*q*, *Me*C=CH_2), 12.38, 10.51 (2*q*, *Me*C(3), *Me*C(4)).

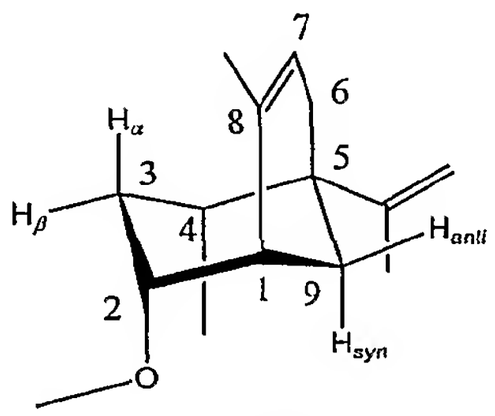
MS (EI): 218 (27), 203 (7), 190 (8), 175 (9), 161 (12), 147 (17), 133 (59), 119 (100), 105 (75), 95 (13), 93 (67), 91 (85), 77 (52), 69 (7), 55 (65), 41 (65).

IR: ν_{max} 2968, 2927, 1708, 1677, 1638, 1446, 1381, 1351, 1238, 1210, 1152, 1103, 1083, 1059, 1003, 889, 830, 802, 790, 659 cm^{-1}.

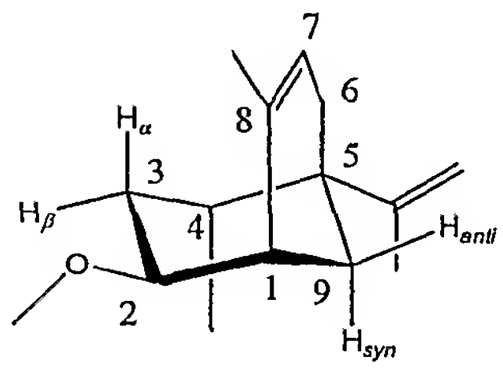
$[a]_D^{22}$ = -768.6 (c=0.97, EtOH)

Odour description: fruity, peppery, woody, elemi, gurjun, ambery

Example 12: 4,8-Dimethyl-5-isopropenyl-8-methoxy-bicyclo[3.3.1]non-7-ene (**12A** and **12B**)



12A



12B

A soln. of 2.9 g of 5-isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-ol (14.1 mmol, α/β 58:42) in 30 ml DMF was added dropwise to a suspension of 0.84 g 55-65% sodium hydride (21 mmol, 1.5 eq.) in 30 ml DMF and the resulting mixture was stirred 1.5 h at 25°C, treated with 2.6 ml methyl iodide (41.8 mmol, 3 eq.), heated 4.5 h at 80°C, poured into 50 ml HCl 2M, and extracted with 2X80 ml hexane. The org. phases were washed with 2X100 ml 1:1 aq. sat. NaCl soln./H_2O, dried, and concentrated. FC (hexane/MTBE 15:1) of the crude (2.17 g) gave 0.25 g **12A** (8.1%), 0.85 g **12B/12A** (55:45, 27.4%), and 1.07 g **12B** (34.5%).

(1*S**2*R**4*S**5*R**)-4,8-Dimethyl-5-isopropenyl-8-methoxy-bicyclo[3.3.1]non-7-ene (**12A**)

Boiling point: 80°C at 0.08 mbar.

^{1}H-NMR (400MHz, $CDCl_3$): δ5.46 (*tq*, J = 1.4, 3.2, H-C(7)), 4.64-4.62 (*m*, C=CH_2), 3.33 (*s*, MeO), 3.29 (*dt*, J = 2.8, 2.9, H-C(2)), 2.41-2.37 (br. *s*, H-C(1)), 2.11 (*dd*, J = 3.0, 12.5, H_{syn}-C(9)), 2.08-2.05 (*m*, C(6)H_2), 1.81 (*ddd*, J = 3.6, 5.8, 14.6, H_α-C(3)), 1.74 (br. *quintet*, J = 7.0, H-C(4)), 1.69 (*td*, J = 1.6, 2.1, MeC(8)), 1.65 (br. *t*, J = 0.9, *Me*C=CH_2),

1.63 (*ddt*, J = 1.5, 1.8, 15.0, H_{β}-C(3)), 1.33 (br. *d*, J = 12.5, H_{anti}-C(9)), 0.91 (*d*, J = 7.2, MeC(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ 153.16 (*s*, C(5)*C*=), 135.24 (*s*, C(8)), 124.13 (*d*, C(7)), 107.26 (*t*, CH_2=), 77.51 (*d*, C(2)), 56.11 (*q*, MeO), 40.59 (*d*), 39.54 (*t*, C(6)), 39.26 (*s*, C(5)), 36.46 (*d*), 28.29 (*t*, C(9)), 24.85 (*t*, C(3)), 22.34 (*q*, *Me*C(8)), 18.06 (*q*, *Me*C=CH_2), 17.92 (*q*, *Me*C(4)).

MS (EI): 220 (4), 205 (1), 188 (18), 173 (10), 159 (3), 145 (8), 133 (34), 119 (17), 107 (17), 105 (32), 93 (24), 91 (32), 85 (100), 77 (20), 71 (6), 55 (19), 41 (26).

IR: ν_{max} 2962, 2925, 2889, 2826, 1638, 1447, 1375, 1193, 1160, 1118, 1108, 1097, 1081, 970, 959, 924, 886, 829, 804, 786 cm^{-1}.

$[a]_D^{22}$ = -90.8 (c=0.14, EtOH)

Odour description: woody, ambery

(1*S**2*S**4*S**5*R**)-4,8-Dimethyl-5-isopropenyl-8-methoxy-bicyclo[3.3.1]non-7-ene (**12B**)

Boiling point: 80°C at 0.08 mbar.

^{1}H-NMR (400MHz, $CDCl_3$): δ 5.55 (*tq*, J = 1.6, 3.2, H-C(7)), 4.62 (*quintet*, J = 1.4, H_t-CH=), 4.57-4.56 (br. *s*, H_c-CH=), 3.49 (*dt*, J = 4.2, 11.6, H-C(2)), 3.36 (*s*, MeO), 2.66-2.62 (br. *s*, H-C(1)), 2.10-2.00 (m, C(6)H_2), 1.95-1.85 (br. *quintet*, J ≈ 7.1, H-C(4)), 1.81 (*td*, J = 5.4, 12.2, H_{α}-C(3)), 1.76 (*dt*, J = 1.6, 2.2, MeC(8)), 1.74 (dd, J ≈ 2.8, 13.0, H_{syn}-C(9)), 1.64 (*dd*, J = 0.5, 1.3, *Me*C=CH_2), 1.59 (*ddd*, J = 1.8, 3.9, 12.8, H_{anti}-C(9)), 1.56 (*dddd*, J = 1.4, 2.0, 4.2, 12.6, H_{β}-C(3)), 0.79 (*d*, J = 7.2, MeC(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ 152.58 (*s*, C(5)*C*=), 134.29 (*s*, C(8)), 123.66 (*d*, C(7)), 107.46 (*t*, CH_2=), 78.58 (*d*, C(2)), 55.98 (*q*, MeO), 40.00 (*t*, C(6)), 39.06 (*s*, C(5)), 38.53 (*d*), 37.11 (*d*), 31.72, 29.58 (2 *t*, C(9),C(3)), 24.42 (*q*, *Me*C(8)), 18.35 (*q*, *Me*C=CH_2), 16.43 (*q*, *Me*C(4)).

MS (EI): 220 (5), 205 (1), 188 (19), 173 (10), 159 (3), 145 (8), 133 (31), 119 (16), 107 (15), 105 (29), 93 (22), 91 (30), 85 (100), 77 (18), 71 (5), 55 (18), 41 (23).

IR: ν_{max} 2965, 2935, 2890, 2828, 1638, 1451, 1374, 1194, 1176, 1103, 1040, 1011, 975, 945, 923, 887, 820, 793, 625 cm^{-1}.

$[a]_D^{22}$ = -195.4 (c=0.76, EtOH)

Odour description: woody, ambery, fatty, green

Example 13: A fragrance composition for shower gel

compound/ingredient	parts by weight 1/1000
Armoise oil	5
Grisalva (5,5,9-Trimethyl-1-ethyltricyclo[8.4.0.0-4,9]-14-oxatetradecane)	5
Clary sage oil	10
Jasmonyl (1,3-Nonanediol acetate)	10
Limette oil	10
Patchouli oil	10
Piconia (Isolongifolanone)	10
Verbena oil Africa	10
Oakmoss absolute Tyrol at 50% in DPG	20
Geranium oil	25
Rosemary oil	25
Sandela (3-Isocamphylcyclohexanol)	25
Lavandin Grosso oil	30
Cinnamon leaves oil	30
Juniper oil	30
Methyl cedryl ketone	30
Dimyrcetol	40
Fixolide (7-Acetyl-1,1,3,4,4,6-hexamethyltetralin)	40
Lilial (p-tert.Butyl-alpha-methyldihydrocinnamic aldehyde)	40
Neroli essential oil	45
Bornyl acetate	50
Cedryl acetate	50
Para-tert-butylcyclohexyl acetate	50
Hydroxy citronellal	50
Irisantheme (alpha-Isomethylionone)	50
Linalyl acetate	65
Galaxolide 50% Benzyl benzoate	65
Lemon oil Italy	70
Bergamot oil	90
5-Isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-one (1)	10
	1000

Adding 5-Isopropenyl-4,8-dimethylbicyclo[3.3.1]non-7-en-2-one (1) to the fragrance composition adds a sophisticated woody-ambery note with fruity (raspberry) undertones. It also imparts more volume to the woody accord in a fir balsam direction.